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DECLARATION

I, **Mrs. MCKEAG, of A.R.T International BP 18 95410 GROSLAY France**

do hereby declare that I am conversant with the English and French languages and am a competent translator thereof.

I declare further that the following is a true and accurate translation into English of the French Patent Application N° 99 08 474 filed on July 01, 1999.

Signed this 18th day of December 2003

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PATENT

CERTIFICATE OF UTILITY - CERTIFICATE OF ADDITION

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Issued in Paris, on : .... 08 DEC 2003

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on behalf of the General Director
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PATENT *cerfa n° 11354*01*
CERTIFICATE OF UTILITY
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1. NAME AND ADDRESS OF APPLICANT OR AGENT TO WHOM CORRESPONDENCE IS TO BE SENT

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TITLE OF INVENTION (no more than 200 characters or spaces)

METHOD FOR DEPOSITING A SILICON-CONTAINING DIELECTRIC MATERIAL ON COPPER

3 APPLICANT(s) SIREN No. APE-NAF code
Name and first names (underline surname) or company name Legal form

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Public undertaking with a scientific, technical and industrial nature

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If more space needed, continue on a separate sheet

4 INVENTOR(S) The inventors are the applicants ☐ yes ☒ no In this case provide a separate inventor designation

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8 **SIGNATURE OF APPLICANT OR AGENT** **(name and capacity of signatory)** **J. LEHU** **422-5/S002**	OFFICIAL SIGNATURE ON RECEIPT			SIGNATURE ON REGISTRATION OF THE APPLICATION AT THE INPI	

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PATENT CERTIFICATE OF UTILITY

DESIGNATION OF THE INVENTOR
(if the applicant is not the inventor or the sole inventor)

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TITLE OF THE INVENTION

METHOD FOR DEPOSITING A SILICON-CONTAINING DIELECTRIC MATERIAL ON COPPER

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PARIS 1st JULY 1999

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422-5/S002

DOCUMENT COMPRISING MODIFICATIONS

PAGES OF DESCRIPTION OR CLAIMS OR DRAWINGS			CM*	DATE OF CORRESPONDENCE	DATE STAMP OF CORRECTOR
Modified	Deleted	Added			
Page 9 to 13		14		17-09-99	18 Feb 2000 LEM

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METHOD FOR DEPOSITING A SILICON-CONTAINING DIELECTRIC MATERIAL ON COPPER

Technical field

The present invention relates to a method for depositing a silicon-containing dielectric material on copper. It particularly relates to a method for depositing a copper-diffusion barrier layer, containing silicon, on copper conductor lines. This method is especially suitable for producing copper interconnection levels on semiconductor devices.

State of the prior art

In production techniques for microelectronic devices, copper is increasingly used in the fabrication of interconnections due to its electric properties and in particular to its very low resistivity. By replacing aluminium it can improve the performances of integrated circuits of the microprocessor type.

For devices fabricated from a silicon substrate, the insulating materials used between the interconnection lines and between the interconnection levels contain silicon. These are SiO_2, SiN and SiON in particular.

The main difficulty related to the use of copper in such devices lies in the fact that a contamination by the copper of the active parts of the substrate (transistors for example) at very low levels (in the order of a few 10^{11} atoms/cm^3) is sufficient to fully degrade the performances of the corresponding circuits. Any diffusion of the copper towards the active parts must therefore be avoided. For this purpose, diffusion barrier layers made of dielectric material are known to

be deposited between the copper and the active parts. Some barrier layers are deposited directly on the copper. The adhesion of the barrier layer material to the copper must also be of good quality to enable the fabrication of interconnections at several levels. The best dielectric materials for producing a copper-diffusion barrier layer are compounds containing silicon and nitrogen, of the SIN_x type.

Materials of the SiN_x type may be deposited at relatively low temperature by methods of CVD type (Chemical Vapour Deposition) using gas mixtures with variable proportions of silane, nitrogen and ammonia. The rate of deposit is accelerated by using a plasma to decompose the reactive species.

The copper may then in turn be contaminated by the material of the barrier layer on account of the method of deposit used. The result is a very marked change in the resistivity of the copper lines. This increase in resistivity increases as the temperature at which the depositing operation is conducted increases. This is the case in particular for inter-level deposits on copper.

The increase in the resistivity of copper can be accounted for by the rapid diffusion of silicon from the material of the barrier layer into the copper. A contamination formed of only 1 % silicon in solution in the copper leads to a twofold increase in the resistivity of copper, which is considerable.

Other layers of dielectric material may be deposited on the copper using precursors containing chemical elements able to contaminate copper. In addition to silicon, fluorine and carbon may be cited.

To deposit a dielectric containing silicon, silane, dimethylsilane or trimethylsilane may be used. Possible contamination of the copper by fluorine may be made by using a CF_x/CH_x mixture as precursor.

When silicon nitride is deposited on copper, the formation of a silicide on the copper surface has been found and used to improve the adhesion of the nitride layer to the copper. Patent US-A-5 447 887, which uses this effect, only mentions the deterioration of the resistance per unit area of the copper layer: the formation of copper silicide leads to a copper consumption 10% less than the initial layer. However, the effect on the resistivity through the silicon being placed in solution in the remainder of the copper layer is not approached. Moreover, this method for improving the adhesion of the nitride to the copper requires the consumption of part of the initial copper layer, which limits its application to relatively thick layers (at least 1 µm thick).

Patent US-A-5 831 283 discloses that the adhesion of the SiN dielectric to copper may be obtained by depositing dense SiN at low temperature and without ammonia. The formation of a silicide is not mentioned as adhesion vector. However, the rate of the nitride deposit is too slow (26 nm/min at 200°C) which penalises productivity. This patent does not refer to any possible degradation of the resistivity of the copper underlying the nitride layer.

Description of the invention

To overcome the disadvantages mentioned above, the present invention puts forward a method for depositing dielectric material on copper, this method making it

possible to prevent the contamination of the copper by a contaminating element derived from a gas used to make this deposit of dielectric material, and with which it is also possible to obtain a good quality interface between the copper and the deposited dielectric material.

The subject of the invention is therefore a method for depositing a dielectric material on copper visible on the surface of a structure, which entails the following steps:

- placing the structure in a CVD (chemical vapour deposition) type deposition chamber,
- adding to the chamber a first gas forming a precursor for the formation of the dielectric material and containing an element able to contaminate copper,
- adding to the chamber a second gas containing a chemical element intended, together with the element contained in the first gas and able to contaminate copper, to form the said dielectric material, the second gas being able to react with the first gas to give the deposit of dielectric material,
- making the deposit of dielectric material from the first gas and the second gas,

characterised in that the method comprises a step for adding a third gas able to prevent contamination of the copper by the said element contained in the first gas.

Advantageously, the deposition chamber permitting plasma enhanced chemical vapour deposition (PECVD), the method comprises a plasma ignition step to conduct the deposit of dielectric material from the first gas and the second gas.

The first gas may be silane. The second gas may contain a chemical element which is nitrogen or it may itself be nitrogen. The third gas may contain oxygen and/or nitrogen and/or carbon. It may be chosen from the group made up of N_xO_y, C_xH_y, a xN_2+yH_2 mixture or a xO_2+yN_2 mixture. By way of example, it may be formed of NH_3, N_2O, CH_4 and C_2H_6.

According to one variant embodiment, the first, second and third gases are also added before ignition of the plasma, the flow rates of the first, second and third gases, the energy needed for deposit and the time of formation of the deposit being adjusted in relation to the desired thickness of dielectric material and its desired physical properties (optical, density, stress, dielectric constant value).

According to another variant embodiment, the steps are conducted in the following order:

- placing the structure in the deposition chamber,
- adding the third gas to the deposition chamber, the third gas being chosen to reduce the oxides present on the copper surface,
- ignition of a third gas plasma in the deposition chamber in order to reduce the said oxides,
- adding the first and second gases to the deposition chamber, adjusting the flow rates of the first, second and third gases, the energy needed for the deposit, and the time of formation of the deposit in relation to the desired thickness of dielectric material and its desired physical properties.

The third gas may advantageously be ammonia.

To obtain a dielectric material in SiN, the first gas may be silane, the chemical element of the second gas may be nitrogen and the third gas may be ammonia.

The formation of the dielectric material may be made at a temperature of between 100 and 600°C, preferably at a temperature in the region of 400°C.

Optionally, the third gas may be the same as the second gas. It may also be a mixture. For example, it may be diluted in a neutral gas such as nitrogen, argon or helium.

Another subject of the invention is the application of this method to the deposition of a copper-diffusion barrier layer on the surface of a structure comprising at least one copper conductor line.

Yet another subject of the invention is the application of this method to the deposition of copper-diffusion barrier layers at the time of fabricating copper interconnection levels on semiconductor devices.

Brief description of the drawings

The invention will be better understood and other advantages and particular features will become apparent on reading the following description that is given by way of example and is non-restrictive, accompanied by the appended drawings among which:

- Figure 1 illustrates the copper plating deposition step in the fabrication of an interconnection level of the damascene type,
- Figure 2 illustrates the mechanical-chemical polishing step in the fabrication of the interconnection level of the damascene type,

- Figure 3 shows the interconnection level after depositing different layers of dielectric material.

Detailed description of embodiments of the invention

Figure 1 shows part of a silicon substrate 1 comprising an electric contact 2 to be connected to a copper electrical line. The electrical contact 2 is laterally surrounded by a dielectric material 6, for example made of SiO_2. In a known manner, a layer of dielectric material 3, for example made of SiO_2, is deposited on the free surface of the structure. Layer 3 is etched such as to expose part of contact 2. A TiN layer 4 is deposited on the etched layer 3. Layer 4 prevents the diffusion of copper into the dielectric and into the silicon substrate 1. Copper plating 5 is then uniformly deposited on layer 4. This plating ensures the electric connection with contact 2 and extends above the layer of dielectric material 3.

Figure 2 shows the structure 10 obtained after the mechanical-chemical polishing step which is continued until the layer of dielectric material 3 is reached and the TiN layer above layer 3 is thus removed. After the polishing step, the polished surface of structure 10 is cleaned. It shows a visible copper mass 15.

Figure 3 shows the interconnection level that is subsequently made. It is an interconnection level of the double damascene type. It comprises an SiN layer 11 deposited on the surface of structure 10, an SiO_2 layer 12 covering layer 11, an SiN layer 13 covering layer 12 and an SiO_2 layer 14 covering layer 13. Layers 11 to 14 may be deposited at a temperature of 400°C.

SiN layer 11, according to the depositing method disclosed in document US 5 831 283, was deposited in the following manner. Gases N_2 and SiH_4 are mixed for 10 seconds in a PECVD deposition chamber. A first deposit is made at 500 W with this mixture. A second deposit is then made at 625 W at the start of which the gas NH_3 is added. This method according to the prior art induces an increase of 40% in the surface resistance of the copper over a thickness of 200 nm.

According to the invention, the increase in the surface resistance of the copper is prevented by adding the NH_3 gas before adding the SiH_4 and N_2 gases in the described example and before ignition of the deposit plasma. The nitrogen enables homogenisation of the temperature and the gas phase. The first deposit of the method according to document US 5 831 283 is eliminated.

It was found that with the method of the invention, a good quality SiN/Cu interface is obtained: the nitride shows no abnormal roughness and no delamination. The properties of the SiN layer are identical to those of the method according to the prior art. Above all, no increase in the surface resistance of the copper is observed, that is to say that if there is an increase in resistance, it is less than 1%.

A variant embodiment of the method will be described below. With this variant it is possible to ensure good reproducibility of the Cu/SiN interface by means of a treatment with NH_3 plasma on the copper surface. This treatment leads to reducing the oxides formed on the surface of the copper.

In this case, in order to prevent reaction of the silane on the copper surface activated by the plasma of

NH_3, and in order to prevent contamination of the copper by the silicon, the SiN deposit must be made as a continuation of the NH_3 plasma treatment. Once the plasma has been ignited with NH_3 gas and the deoxidation treatment has been completed, the silane and nitrogen gases are added and the ammonia flow rate is modified to obtain the necessary proportions of gases for depositing silicon nitride. The NH_3 plasma is made at the same temperature as the nitride deposit. The power of the NH_3 plasma may be different to that of the nitride deposit. It only needs to be adjusted without the plasma being interrupted.

CLAIMS

1. Method for depositing a dielectric material (11) on copper (15) visible on the surface of a structure (10), entailing the following steps:

- placing the structure (10) in a CVD (chemical vapour deposition) type deposition chamber,
- adding to the chamber a first gas forming a precursor for the formation of the dielectric material and containing an element that could contaminate copper,
- adding to the chamber a second gas containing a chemical element intended to form the said dielectric material (11) in combination with the element contained in the first gas and that could contaminate copper, the second gas being able to react with the first gas to cause the deposition of the dielectric material (11),
- performing the deposition of dielectric material from the first gas and the second gas,

characterised in that the method comprises a step for adding a third gas able to prevent the contamination of copper by the said element contained in the first gas.

2. Method according to claim 1, characterised in that, the deposition chamber enabling plasma enhanced chemical vapour deposition (PECVD), the method comprises a step for igniting the plasma to deposit dielectric material from the first gas and the second gas.

3. Method according to either of claims 1 or 2, characterised in that the first gas is silane, the contaminating element being Si.

4. Method according to either of claims 1 or 2, characterised in that the said chemical element of the second gas is nitrogen.

5. Method according to either of claims 1 or 2, characterised in that the second gas is nitrogen.

6. Method according to either of claims 1 or 2, characterised in that the third gas contains oxygen and/or nitrogen and/or carbon.

7. Method according to claim 6, characterised in that the third gas is chosen from the group made up of N_xO_y, C_xH_y, a xN_2+yH_2 mixture or a xO_2+yN_2 mixture.

8. Method according to claim 6, characterised in that the third gas is chosen from the group made up of NH_3, N_2O, CH_4 and C_2H_6.

9. Method according to either of claims 1 or 2, characterised in that the first, second and third gases are also added before igniting the plasma, the flow rates of the first, second and third gases, the energy required for deposition and the time of formation of the deposit being adjusted in relation to the desired thickness of the dielectric material (11) and its desired physical properties.

10. Method according to claim 2, characterised in that the steps are conducted in the following order:

- placing the structure (10) in the deposition chamber,
- adding the third gas to the deposition chamber, the third gas being chosen to reduce the oxides present on the surface of the copper (15),
- ignition of a plasma of a third gas in the deposition chamber in order to reduce the said oxides,
- adding the first and second gases to the deposition chamber, adjusting the flow rates of the first, second and third gases, the energy required for the deposit and the formation time of the deposit in relation to the desired thickness of the dielectric material (11) and its desired physical properties.

11. Method according to claim 10, characterised in that the third gas is ammonia.

12. Method according to either of claims 1 or 2, characterised in that, for the purpose of obtaining an SiN dielectric material, the first gas is silane, the said chemical element of the second gas is nitrogen and the third gas is ammonia.

13. Method according to any one of claims 1 to 12, characterised in that the dielectric material (11) is formed at a temperature of between 100 and 600°C.

14. Method for depositing a dielectric material (11) on copper (15) visible on the surface of a structure (10), entailing the following steps:

- placing the structure (10) in a CVD (chemical vapour deposition) type deposition chamber,
- adding to the chamber a gas forming a precursor for the formation of the dielectric material (11) and containing a first element able to contaminate copper and a second element able to combine with the first element to give the dielectric material (11),
- depositing the dielectric material by combining the first element and the second element,

characterised in that the method comprises a step for adding an additional gas able to prevent the contamination of the copper by the said element contained in the precursor gas.

15. Method according to claim 14, characterised in that, the deposition chamber enabling plasma enhanced chemical vapour deposition (PECVD), the method comprises a plasma ignition step to deposit the dielectric material from the precursor gas.

16. Method according to either of claims 14 or 15, characterised in that, in order to obtain an SiC dielectric material, the said gas forming a precursor is trimethylsilane.

17. Application of the method according to any one of the preceding claims to the deposition of a copper-diffusion barrier layer on the surface of a structure (10) containing at least one copper conductor line (15).

18. Application of the method according to any one of claims 1 to 16 to the deposition of copper-diffusion

barrier layers when producing copper interconnection levels on semiconductor devices.

English translation of the amended sheets

It was found that with the method of the invention, a good quality SiN/Cu interface is obtained: the nitride shows no abnormal roughness and no delamination. The properties of the SiN layer are identical to those of the method according to the prior art. Above all, no increase in the surface resistance of the copper is observed, that is to say that if there is an increase in resistance, it is less than 1%.

A variant embodiment of the method will be described below. With this variant it is possible to ensure good reproducibility of the Cu/SiN interface by means of a treatment with NH_3 plasma on the copper surface. This treatment leads to reducing the oxides formed on the surface of the copper.

In this case, in order to prevent reaction of the silane on the copper surface activated by the plasma of NH_3, and in order to prevent contamination of the copper by the silicon, the SiN deposit must be made as a continuation of the NH_3 plasma treatment. Once the plasma has been ignited with NH_3 gas and the deoxidation treatment has been completed, the silane and nitrogen gases are added and the ammonia flow rate is modified to obtain the necessary proportions of gases for depositing silicon nitride. The NH_3 plasma is made at the same temperature as the nitride deposit. The power of the NH_3 plasma may be different to that of the nitride deposit. It only needs to be adjusted without the plasma being interrupted.

A further subject of the invention is a method for depositing a dielectric material on copper visible on the surface of a structure, entailing the following steps:

English translation of the amended sheets

- placing the structure in a CVD (chemical vapour deposition) type deposition chamber,

- adding a gas forming a precursor into the chamber for the formation of the dielectric material and containing a first element able to contaminate copper and a second element able to combine with the first element to give the dielectric material,

- depositing the dielectric material by combining the first element and the second element,

characterised in that the method comprises a step for adding an additional gas able to prevent contamination of the copper by the said element contained in the precursor gas.

In order to obtain an SiC dielectric material, the gas forming a precursor may be trimethylsilane.

English translation of the amended sheets

CLAIMS

1. Method for depositing a dielectric material (11) on copper (15) visible on the surface of a structure (10), entailing the following steps:

- placing the structure (10) in a CVD (chemical vapour deposition) type deposition chamber,
- adding to the chamber a first gas forming a precursor for the formation of the dielectric material and containing an element that could contaminate copper,
- adding to the chamber a second gas containing a chemical element intended to form the said dielectric material (11) in combination with the element contained in the first gas and that could contaminate copper, the second gas being able to react with the first gas to cause the deposition of the dielectric material (11),
- performing the deposition of dielectric material from the first gas and the second gas,

characterised in that the method comprises a step for adding a third gas able to prevent the contamination of copper by the said element contained in the first gas.

2. Method according to claim 1, characterised in that, the deposition chamber enabling plasma enhanced chemical vapour deposition (PECVD), the method comprises a step for igniting the plasma to deposit dielectric material from the first gas and the second gas.

English translation of the amended sheets

3. Method according to either of claims 1 or 2, characterised in that the first gas is silane, the contaminating element being Si.

4. Method according to either of claims 1 or 2, characterised in that the said chemical element of the second gas is nitrogen.

5. Method according to either of claims 1 or 2, characterised in that the second gas is nitrogen.

6. Method according to either of claims 1 or 2, characterised in that the third gas contains oxygen and/or nitrogen and/or carbon.

7. Method according to claim 6, characterised in that the third gas is chosen from the group made up of N_xO_y, C_xH_y, a xN_2+yH_2 mixture or a xO_2+yN_2 mixture.

8. Method according to claim 6, characterised in that the third gas is chosen from the group made up of NH_3, N_2O, CH_4 and C_2H_6.

9. Method according to either of claims 1 or 2, characterised in that the first, second and third gases are also added before igniting the plasma, the flow rates of the first, second and third gases, the energy required for deposition and the time for formation of the deposit being adjusted in relation to the desired thickness of the dielectric material (11) and its desired physical properties.

English translation of the amended sheets

10. Method according to claim 2, characterised in that the steps are conducted in the following order:

- placing the structure (10) in the deposition chamber,
- adding the third gas to the deposition chamber, the third gas being chosen to reduce the oxides present on the surface of the copper (15),
- ignition of a plasma of a third gas in the deposition chamber in order to reduce the said oxides,
- adding the first and second gases to the deposition chamber, adjusting the flow rates of the first, second and third gases, the energy required for the deposit and the formation time of the deposit in relation to the desired thickness of the dielectric material (11) and its desired physical properties.

11. Method according to claim 10, characterised in that the third gas is ammonia.

12. Method according to either of claims 1 or 2, characterised in that, for the purpose of obtaining an SiN dielectric material, the first gas is silane, the said chemical element of the second gas is nitrogen and the third gas is ammonia.

13. Method according to any one of claims 1 to 12, characterised in that the dielectric material (11) is formed at a temperature of between 100 and 600°C.

14. Method for depositing a dielectric material (1) on copper (15) visible on the surface of a structure (10), entailing the following steps:

English translation of the amended sheets

- placing the structure (10) in a CVD (Chemical Vapour Deposition) type deposition chamber,

- adding to the chamber a gas forming a precursor for the formation of the dielectric material (11) and containing a first element able to contaminate copper and a second element able to combine with the first element to give the dielectric material (11),

- depositing the dielectric material by combining the first element and the second element,

characterised in that the method comprises a step for adding an additional gas able to prevent contamination of the copper by the said element contained in the precursor gas.

15. Method according to claim 14, characterised in that, the deposition chamber enabling plasma enhanced chemical vapour deposition (PECVD), the method comprises a plasma ignition step to deposit the dielectric material from the precursor gas.

16. Method according to either of claims 14 or 15, characterised in that, in order to obtain an SiC dielectric material, the said gas forming a precursor is trimethylsilane.

17. Application of the method according to any one of the preceding claims to the deposition of a copper-diffusion barrier layer on the surface of a structure (10) containing at least one copper conductor line (15).

18. Application of the method according to any one of claims 1 to 16 to the deposition of copper-diffusion

barrier layers when producing copper interconnection levels on semiconductor devices.